(86) Date de dépôt PCT/PCT Filing Date: 1992/08/18

(87) Date publication PCT/PCT Publication Date: 1993/03/04

(45) Date de délivrance/Issue Date: 2003/07/29

(85) Entrée phase nationale/National Entry: 1994/02/12

(86) N° demande PCT/PCT Application No.: DE 1992/000697

(87) N° publication PCT/PCT Publication No.: 1993/004017

(30) Priorité/Priority: 1991/08/20 (P 41 27 459.8) DE

(51) Cl.Int.^{5}/Int.Cl.^{5} C05G 3/00

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(54) Titre : PROCEDE POUR LA FABRICATION DE GRANULES DE FERTILISANTS RECOUVERTES D'UNE MEMBRANE
(54) Title: PROCESS FOR THE MANUFACTURE OF MEMBRANE-COVERED FERTILIZER GRANULES

____inflow air --- granules	.... catalyst
Temperature	Concentration
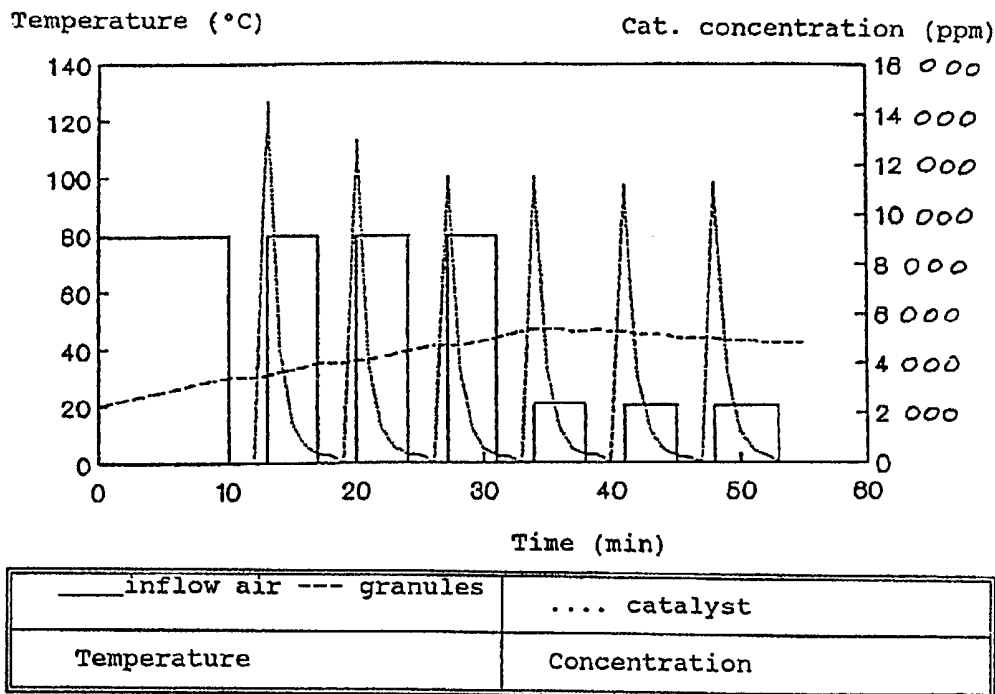
(57) Abrégé/Abstract:
Described is a process for the manufacture of membrane-covered fertilizer granules by coating the granules with films of a mixture of a polyisocyanate and a polyol, the coating compound being applied in proportions such that each film has a thickness of 10 to 30 μm, preferably 15 to 20 μm. The granular fertilizer manufactured in this way has the advantage that it initially emphasizes nitrogen release and subsequently potassium release.

The invention relates to a process for the preparation of membrane-coated fertilizer granules for demand-related plant feeding.

Nowadays, modern, environmentally acceptable and demand-related plant feeding is based to an increasing extent on long-acting fertilizers which are characterised by chemical modification of the nutrients or by coating soluble fertilizer granules.

Coated long-acting fertilizers are described in numerous patents. Urea formaldehyde resins, PE, PP, alkyd resins, epoxy resins and recently polyurethane resins, amongst others, are used as coating agents (e.g., DE 3 544 451, US 3 264 088, GB 1 011 463, EP 0 276 179, DE 2 834 513, US 3 223 518, NL patent 129 279). With the systems mentioned, it has proved more or less possible to modify the nutrient releases over time so that release periods can be achieved for fairly short or fairly long growing times.

A disadvantage of the well known methods is that, until now, parameters for demand-related plant feeding, e.g., homogeneity of the individual particle coating, physical resilience, frost resistance, could be solved only incompletely, if at all. In particular, it has not been possible hitherto to control the release of individual nutrients from special salt mixtures in such as way that e.g., the release of potassium is delayed to a greater extent compared with nitrogen.

The aim of the invention is to overcome the well known disadvantages. An economic, industrial production process has now been found which, with sufficient homogeneity of the individual particle coating, makes it possible to produce physically resilient, frost-resistant granulated material from which the controlled, delayed release of nutrients takes place as defined by Fick's laws of diffusion.

An important prerequisite for obtaining high mechanical resilience is the selection of a highly resilient coating

material which, when it is applied to the fertilizer granules, shows its mechanical properties to their best advantage.

A solvent-free two-component polyurethane resin system that can be processed at room temperature and which can be cured by amine catalysis within very short periods (compare DE 3544 451) has proved to be suitable for coating according to the invention.

The coating process according to the invention is carried out in a drum which is provided with special attachments. On the one hand, specially shaped mixing blades ensure the homogeneity of the mixture, and on the other hand air channels lead into the bed of granulated material so as to be able to aerate said bed intensively. The reaction takes place in a closed system.

The granules for said coating process must be largely spherical, low-dust, attrition-resistant, break-proof and the nutrients contained therein must be largely water-soluble. A narrow particle size distribution of the granules is advantageous, the factor 3 between the smallest and the largest particles of granulated material being sufficient.

A coating process is described in DE 35 44 451 in which, with a planned granulated material coating of 15% by wt. coating, based on the end product, the coating compound composed of poly-isocyanate and polyol is deposited 3 times in 5% portions with simultaneous permanent catalyst gassing with amine-saturated nitrogen gas at 20 °C. The outcome of such a coating leads to an initial release of up to 18% after 24 hours (example 1).

The release of electrolytes from plastics-coated fertilizers in an aqueous solution is determined by measuring the conductivity.

To this end, 10.0 g of the sample to be tested are added to 800 ml of water with a conductivity of less than 0.5 μs/cm. The water is stirred for t days at a constant rate of rotation of 300 rpm at 25 °C. The change in the salt content of the solution

after t days is determined by conductimetry.

In order to draw up a calibration curve, the conductivity is measured in solutions with 0.2; 0.4; 0.6; 0.8; 1.0; 2.0; 4.0; 6.0; 8.0 and 10.0 g of dissolved sample in 800 ml of water, the conductivity being measured in mS/cm.

The rate of release R is then determined on the basis of the calibration curve, the mean rate of release per day R_m being determined by $R_{t2} - R_{t1}/t2 - t1$ where R_{t1} = rate of release after t1 days and R_{t2} = rate of release after t2 days.

Although the basic flow characteristic curve reveals a delay in nutrient release, it does not give all the indications of the presence of a true membrane. The following are to be regarded as indices of membrane-controlled diffusion (membrane function):

a)   a measurable membrane activation time and

b)   the applicability of Fick's law of diffusion according to the following differential equation:

$$\frac{dmi}{dt} = - K \times \frac{1}{n(T)} \times \frac{\Delta ci\ (T)}{f\ (ri)} \times \frac{F}{D} \times T$$

mi   molar concentration of the substance i

t   time

K   constant: $R/(6 \pi N)$ R: gas constant

N: Avogadro's constant

n(T)   Viscosity membrane/solution (substance property of the coating if well executed)

Δci(T)   Concentration gradient of the substance i (substance property of the core composition)

f(ri)   Velocity factor of the particle i with the radius r (substance property of the core composition)

F   Membrane surface area (particle size distribution and surface structure of the granules)

D   Membrane thickness (effective thickness of coating deposited)

T   Temperature in °Kelvin

The release of the nutrients in the time unit is dependent not only on the total membrane surface, the membrane thickness and the temperature but also essentially on the concentration difference between the individual dissolved substances inside the coated granules and the solution surrounding the granules.

Surprisingly, it has now been found that if the process is carried out in a particular way it is possible to produce granules which, in terms of their release characteristics, exhibit all the typical features of membrane-controlled diffusion. With the process according to the invention, coated granules were obtained which have a measurable characteristic membrane activation time. The subsequent nutrient release likewise confirms the active separation of the reserve of active substances from the surrounding solution.

In order to produce this complete membrane as a diffusion regulator, the coating material to be applied consisting of polyisocyanate and polyol is metered in such a way that layer thicknesses of 10 to 30 μm, preferably 15 to 25 μm are not exceeded. In the case of a granulated material in the particle size range of 2 to 4 mm and a median value of 3.0 mm, this means a partial quantity of approx. 1 to 3% to be deposited, particularly less than 2% by mass, based on the mass of granules to be coated.

After a defined distribution and spreading time, this proportion of coating compound is caused to react spontaneously by means of a highly concentrated amine mist as catalyst. The highly concentrated amine mist is produced directly from undiluted amine under airless conditions with a pressure of 2 to 10 bar, preferably 3 to 5 bar, with a volume flow of 10 to 30 ml/s.

In contrast to gassing with only a dilute amine-air mixture, the highly concentrated amine mist makes it possible to create, on all the reaction sites simultaneously, such a high catalyst potential on the entire coating compound deposited that

simultaneous spontaneous curing takes place on each individual particle. As a result, the extremely sensitive gel stage which represents the transition between free-flowing resin mixture and tack-free coating surface will pass through extremely rapidly without destruction of the resin coating that is just in the process of forming.

After the tack-free state has been reached, the amine is removed to such an extent by aeration and degassing prior to the next application of coating compound that premature initiation of the reaction before the next distribution and spreading stage is prevented. This separation of the individual reaction stages according to the invention is important for the dense structure of the individual particle membrane. Imtermediate bonding of individual particles to each other would lead to cracking when the particles separate and hence damage to the surface formed thus far, and would reduce substantially the quality of the coating.

The temperature in the reaction bed affects both the distribution and spreading of the coating and the reaction time. It was found that in a temperature range of 25 to 50 °C, preferably in the region of 30 to 40 °C, spreading and distribution are accelerated sufficiently by a lowering of the viscosity without the reaction time being reduced to the same extent. The amount of catalyst is adjusted i.e. reduced, to the increased temperature whilst maintaining the catalyst potential. Temperature control is achieved by varying the inflow air temperature depending on the process heat released.

After introduction of the amine mist and an appropriate reaction time, aeration is carried out preferably by introducing air directly into the inside of the bed of granulated material. As a result of the rapid gaseous exchange thereby made possible, amine is removed from the bed of granulated material which is thus prepared in an optimum time for the subsequent application of coating compound.

In order to develop the desired membrane thickness, the coating process described is repeated several times. It has become apparent in so doing that at a granulated material temperature of 30 °C at the beginning of the first coating cycle, e.g. by heating with air to an inflow air temperature of about 80 °C, after the third coating application the temperature can be kept in the optimum temperature range of 30 to 40 °C by cooling with inflow air at ambient temperature. At the same time, the amount of amine is reduced in stages. In this way, 2 - 5% by mass based on the coating compound applied, is deposited with dimethyliso-propylamine in the first coating process. This can then be reduced to 0.5% by mass in the further coating stages.

A reproducible production process is ensured in a suitable manner by process control and regulation by SPC (stored program control).

Example 1

Preparation of membrane-coated fertilizer granules with a nutrient release time of 8 months.

450kg of a spherical granulated material NPK 16-10-20 are placed in a sealable drum and heated to a granulated material temperature of 30 °C by passing through a stream of air preheated to 80 °C. Whilst the drum is rotating, 8.8 kg of a polyol-polyisocyanate mixture are applied dropwise to the granules in the first stage and mixed for a total of 2 mins.

Subsequently, without any further inflow of air and the drum being closed, dimethylisopropylamine is applied under airless conditions via two wide-jet nozzles, diameter 0.4 mm, with a pressure of about 4 bar and a volume flow of 18.7 ml/s. After a reaction time of 1 minute, the amine concentration in the bed of granulated material is reduced to below 250 ppm within a further 4 minutes by connecting up inflow air and off-gas in a controlled manner.

The sequence of stages resin application, mixing time, amine application, reaction time and aeration is passed through six times, as can be seen from the table below.

Table

Stage	Resin	Catalyst	Temperature (°C) of	
			inflow air	granules
1.	8.8 kg	0.24 kg	80	30
2.	8.8 kg	0.20 kg	80	33
3.	8.8 kg	0.18 kg	80	35
4.	8.8 kg	0.16 kg	80	38
5.	8.8 kg	0.14 kg	20	38
6.	8.8 kg	0.14 kg	20	36
Total	52.8 kg	1.06 kg		

The coating process with the parameters inflow air and granulated material temperature and catalyst concentration is shown again by way of a graph in figure 1.

The resin membrane produced in this way fulfils the conditions of the Fick diffusion equation given above.

Above all, a measurable membrane activation can be observed which becomes particularly noticeable at low temperatures by a marked delay in the onset of nutrient release, as can be seen from figure 2. The temperature dependence of cumulative nutrient release from the granulated material prepared according to example 1 to be expected from Fick's law of diffusion is shown in this figure.

Figure 3 shows the rate of diffusion as a function of the thickness of the coating surrounding the granules. The granules measured in this figure were prepared with different quantities of resin, as in example 1.

Figure 4 shows the characteristic dissolution behaviour of an NPK 16-10-20 fertilizer on the basis of the individual nutrient solubilities in a closed system with simulation of water ingress and nutrient release, as would be expected in the ideally coated fertilizer core.

Figure 5 shows the actual ratios of nutrient release of the fertilizer granules prepared according to the invention according to example 1.

The change in the NPK ratios during the period of nutrient release of the fertilizer granules coated according to example 1 (figure 5) corresponds to the theoretical expectation (Figure 4). This analytical finding shows that the saturated solution present in the interior of the individual coated particle leads to the same nutrient ratios after membrane penetration into the outside solution.

Figure 6 shows the high degree of homogeneity of the product from the production process according to the invention (similar to example 1 with 4 coating stages) in a comparison between the individual particle measurements of the granulated material A according to the invention and a comparative product B (Osmocote^R, Sierra, Heerlen NL).

In the application of coated long-acting fertilizers which are to be used for supplying substrates, mechanical mixing, storage stability of substrates already supplied in general but also unforeseeable frost effects are important critical factors under practical conditions.

In figure 7 it is shown how the granulated material prepared according to the invention behaves in comparison with other coated products (Osmocote^R, Sierra, Heerlen NL) during storage with and without intermittent frost action. Whilst the comparative product has completely lost its property of delayed nutrient release after frost action, this property is only

slightly impaired with the granulated material prepared according to the invention.

It is shown in figure 8 how the granulated material prepared according to the invention behaves in comparison with other coated products (comparative product as above) in terms of their mechanical resilience during substrate preparation. The nutrient release behaviour of granules produced according to the invention is increased only slightly even with vigorous i.e., repeated mechanical mixing, whereas the comparative product exhibits an unacceptable direct salt release from destroyed granules.

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ABSTRACT OF THE DISCLOSURE

Described is a process for the manufacture of membrane-
covered fertilizer granules by coating the granules with
films of a mixture of a polyisocyanate and a polyol, the
coating compound being applied in proportions such that each
film has a thickness of 10 to 30 μm, preferably 15 to 20 μm.
The granular fertilizer manufactured in this way has the
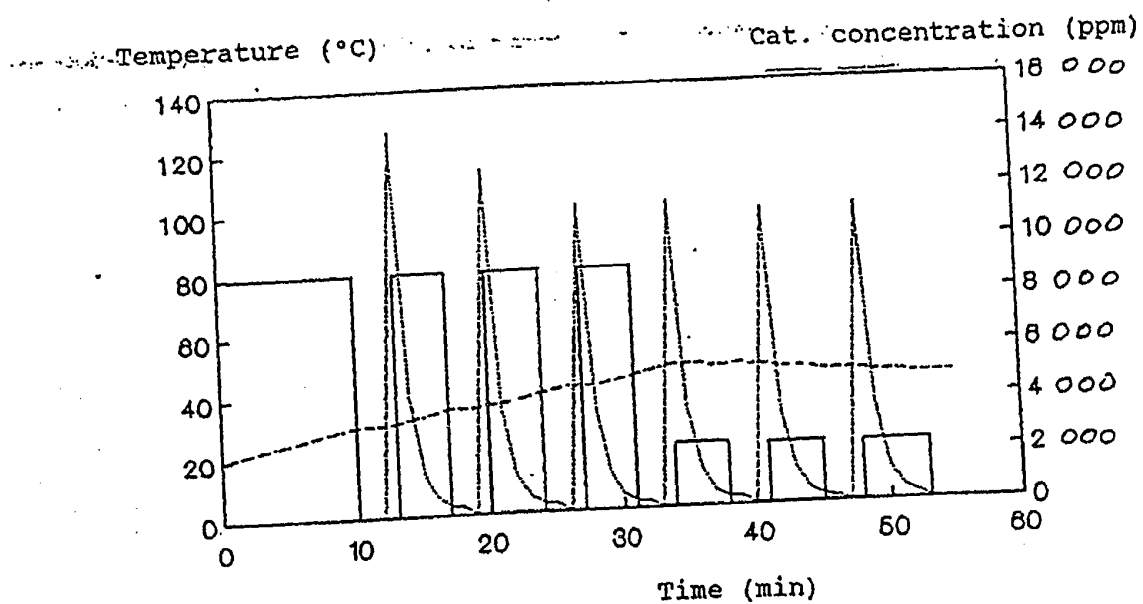advantage that it initially emphasizes nitrogen release and
subsequently potassium release.

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The embodiments of the invention in which an exclusive

property or privilege is claimed are defined as follows:

1. A process for the manufacture of membrane-covered

fertilizer granules in which layers of a mixture of

polyisocyanate and polyol are applied thereto, the layers

each being cured separately with amine nebulized in liquid

form, wherein the mixture is applied in each case within a

temperature range of from 25° to 50°C. and in an amount

such that the individual layers have a layer thickness of

from 10 to 30 µm, and wherein, after the curing of each

layer, the amine concentration is reduced to a level which

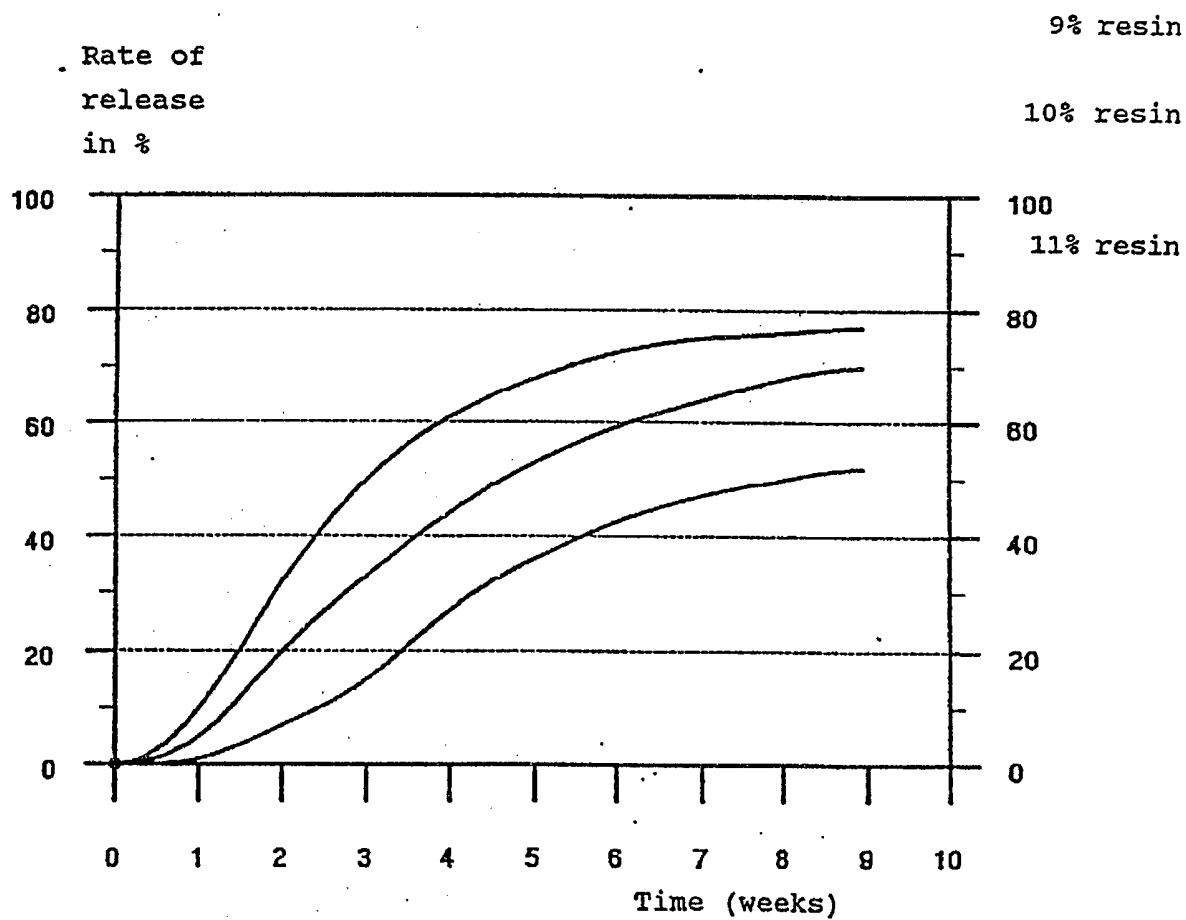is not catalytically active before the next layer is

applied.

Figure 1

Temperature (°C)   Cat. concentration (ppm)

Time (min)

___inflow air --- granules	.... catalyst
Temperature	Concentration

Figure 2

% by
wt.

Time (days)

____15 °C ----25 °C ...40 °C

Figure 3

Figure 3

Rate of release in %

9% resin

10% resin

11% resin

Time (weeks)
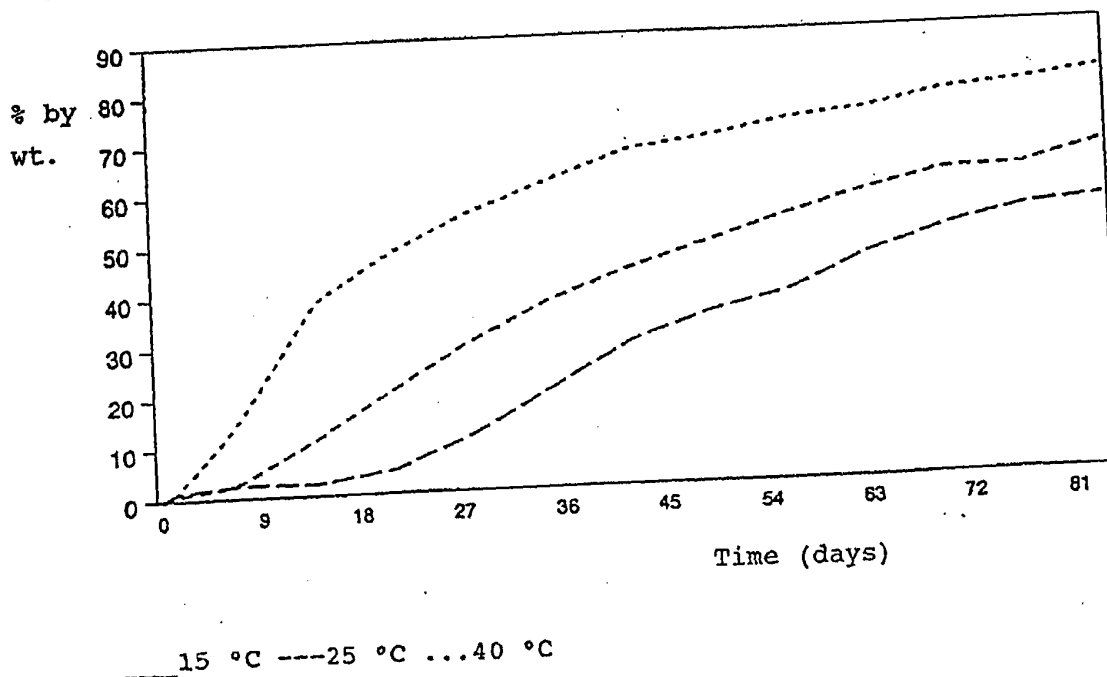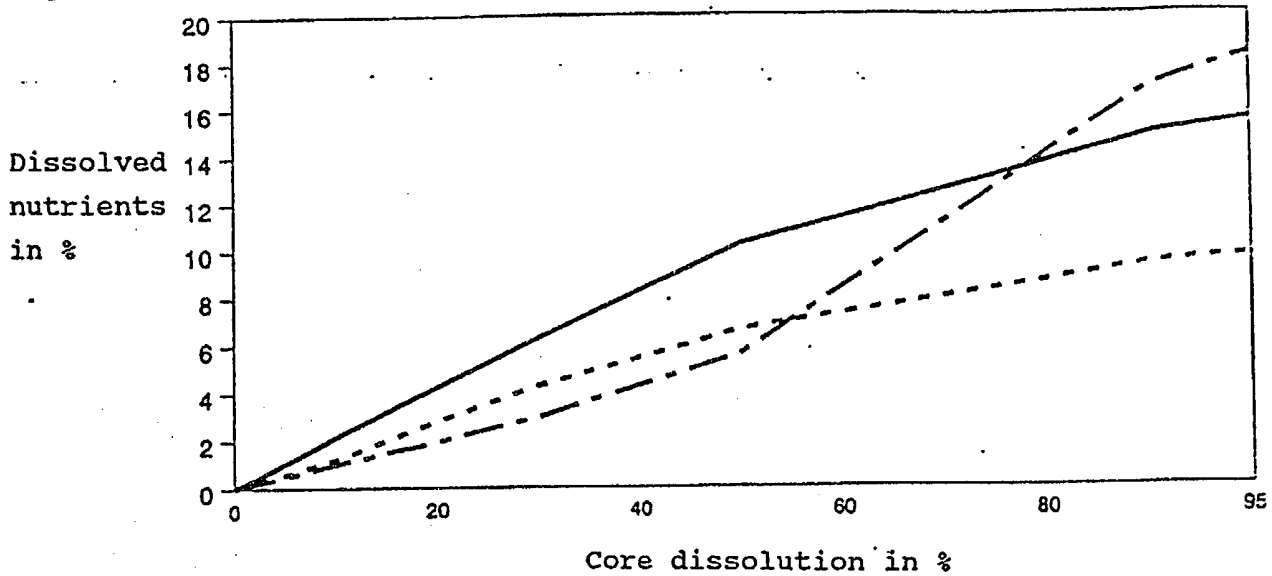
Figure 4

___total N ----P_2O_5 -.-.-. K_2O

Figure 5
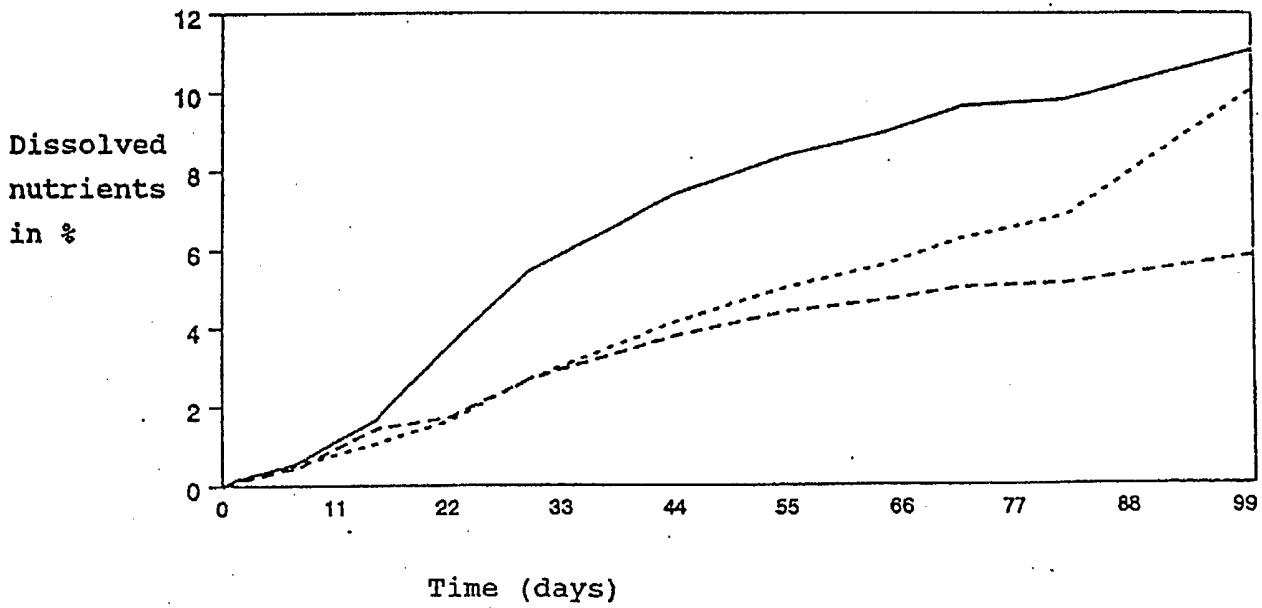
-N ----P_2O_5 ....K_2O

Figure 6

Rate of
release
(%) at
25 °C
cumulative

A

Time (days)

▽ means

Rate of
release
(%) at
25 °C
cumulative

B

Time (days)
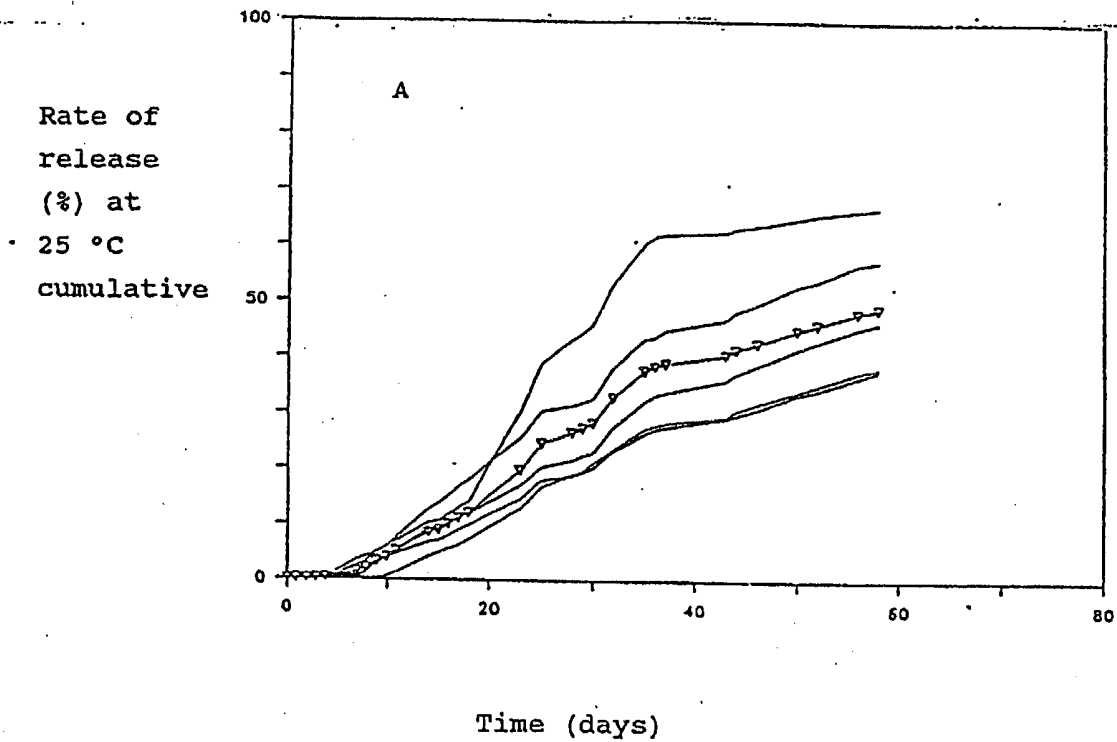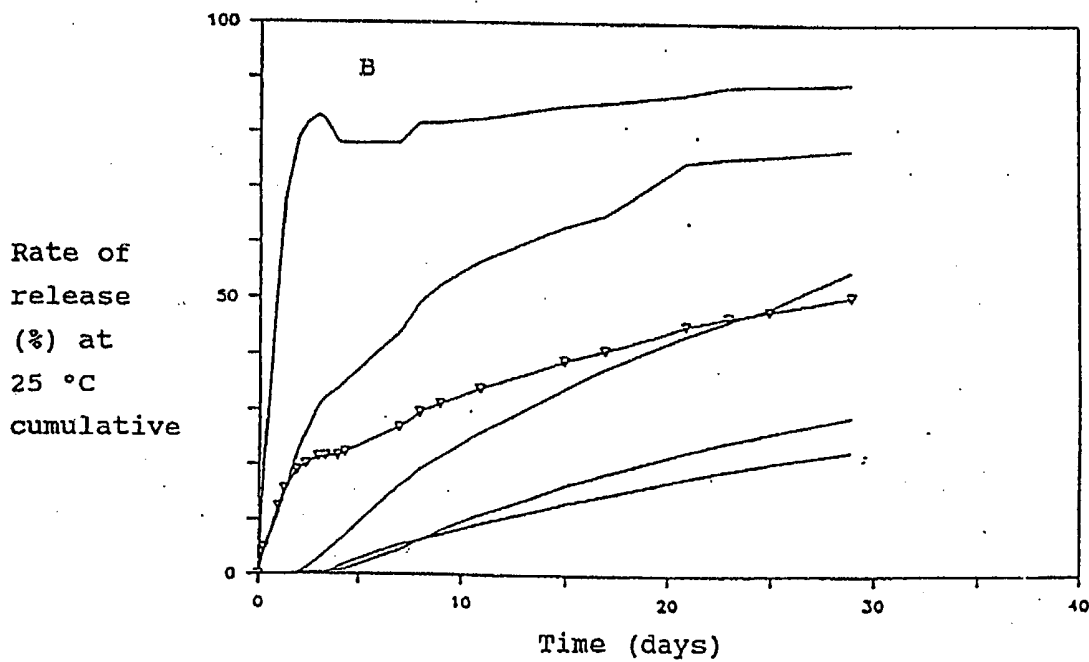
Figure 7

Substrate: peat
Storage temp. ca. 21°C

Storage stability
(in mS/cm)

Storage time (weeks)
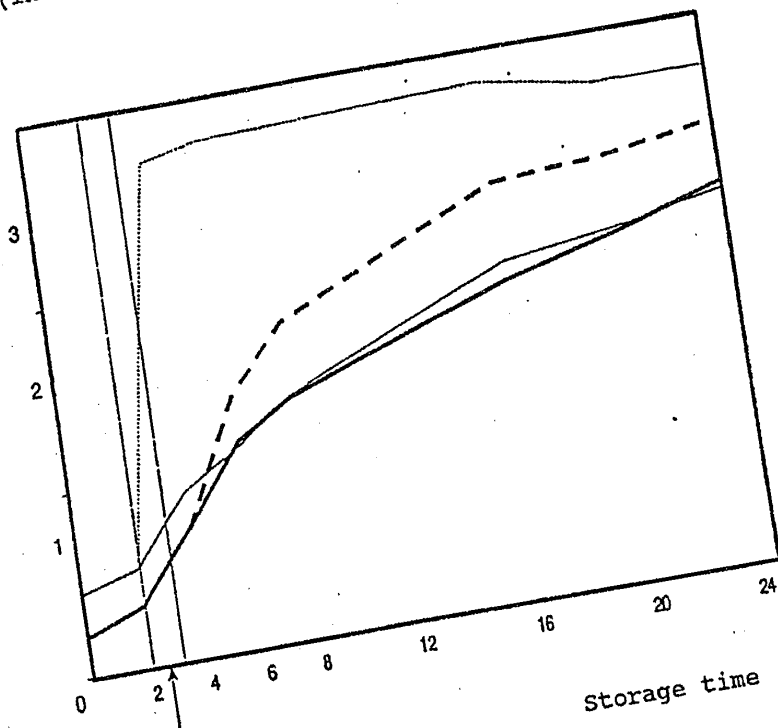
Frost
-10 °C

— without frost --- with frost   — without frost ... with frost
Product according to Example 1   Comparative product

Figure 8

Conductivity (mS/cm)

Substrate: peat

Storage temp. ca. 21°C

2

1

0

2x   4x   2x   4x

Manual mixing Mechanical mixing │ Manual mixing Mechanical mixing

Sample taken 1 week   Sample taken 5 weeks

after the test began

☐ Product according to Example 1   ▧ Comparative product